

Heterogeneous Catalysis and Solid Catalysts

Organometallic Compounds and Homogeneous Catalysis is a separate Keyword

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1. Introduction	3	3.2.5. Supported Sulfide Catalysts	36
1.1. Types of Catalysis	3	3.2.6. Hybrid Catalysts	36
1.2. Catalysis as a Scientific Discipline	4	3.2.7. Ship-in-a-Bottle Catalysts	38
1.3. Industrial Importance of Catalysis	6	3.2.8. Polymerization Catalysts	38
1.4. History of Catalysis	6	4. Production of Heterogeneous Catalysts	39
2. Theoretical Aspects	7	4.1. Unsupported Catalysts	40
2.1. Principles and Concepts	7	4.2. Supported Catalysts	43
2.1.1. Sabatier's Principle	7	4.2.1. Supports	44
2.1.2. The Principle of Active Sites	9	4.2.2. Preparation of Supported Catalysts	44
2.1.3. Surface Coordination Chemistry	10	4.3. Skeletal Catalysts	45
2.1.4. Modifiers and Promoters	11	4.4. Unit Operations in Catalyst Production	46
2.1.5. Active Phase—Support Interactions	11	5. Characterization of Solid Catalysts	48
2.1.6. Spillover Phenomena	12	5.1. Physical Properties	48
2.1.7. Phase-Cooperation and Site-Isolation Concepts	13	5.1.1. Surface Area and Porosity	48
2.1.8. Shape-Selectivity Concept	13	5.1.2. Particle Size and Dispersion	50
2.1.9. Principles of the Catalytic Cycle	14	5.1.3. Structure and Morphology	50
2.2. Kinetics of Heterogeneous Catalytic Reactions	15	5.1.4. Local Environment of Elements	52
2.2.1. Concepts of Reaction Kinetics (Microkinetics)	16	5.2. Chemical Properties	54
2.2.2. Application of Microkinetic Analysis	18	5.2.1. Surface Chemical Composition	54
2.2.3. Langmuir–Hinshelwood–Hougen–Watson Kinetics	18	5.2.2. Valence States and Redox Properties	55
2.2.4. Activity and Selectivity	19	5.2.3. Acidity and Basicity	58
2.3. Determination of Catalytic Mechanisms	21	5.3. Mechanical Properties	60
3. Classification of Solid Catalysts	22	6. Reaction Networks and Mechanisms of Selected Catalytic Reactions on Solid Catalysts	60
3.1. Unsupported (Bulk) Catalysts	23	6.1. Carbon Monoxide Oxidation	61
3.1.1. Metal Oxides	23	6.2. Ammonia Synthesis	61
3.1.1.1. Simple Binary Oxides	23	6.3. Acid–Base catalysis of Hydrocarbon Transformations	62
3.1.1.2. Complex Multicomponent Oxides	25	6.3.1. Introduction	62
3.1.2. Metals and Metal Alloys	31	6.3.2. Carbocations and Their Reactions	64
3.1.3. Carbides and Nitrides	31	6.3.2.1. Nature and Formation of Carbocations	64
3.1.4. Carbons	32	6.3.2.2. Reactions of Carbenium Ions	65
3.1.5. Ion-Exchange Resins and Ionomers	32	6.3.3. Catalytic Reactions Involving Carbocation Intermediates	70
3.1.6. Molecularly Imprinted Catalysts	33	6.4. Metal Catalysis of Hydrocarbon Transformations	75
3.1.7. Metal Salts	33	6.5. Selective Hydrocarbon Oxidation Reactions	78
3.2. Supported Catalysts	33		
3.2.1. Supports	33		
3.2.2. Supported Metal Oxide Catalysts	34		
3.2.3. Surface-Modified Oxides	35		
3.2.4. Supported Metal Catalysts	35		

6.5.1.	Epoxidation of Ethylene and Propene	78	8.1.	Catalytic Reactors	91
6.5.2.	Ammonoxidation of Alkenes	80	8.1.1.	Classification of Reactors	91
6.6.	Hydroprocessing Reactions	81	8.1.2.	Laboratory Reactors	92
7.	Application of Catalysis in Industrial Chemistry	83	8.1.3.	Industrial Reactors	94
7.1.	Important Inorganic Reactions	83	8.1.4.	Special Reactor Types and Processes	99
7.2.	Important Organic Reactions	85	8.2.	Filling Fixed-Bed Reactors	101
7.3.	Petroleum Refining	88	8.3.	Reactor Start-Up	101
7.4.	Production of Synthetic Fuels	89	8.4.	Diffusion, Mass and Heat Transfer Effects	101
7.5.	Pollution Control	89	8.4.1.	Effectiveness Factor	102
7.5.1.	Mobile Sources	89	8.4.2.	Effects on Selectivity	103
7.5.2.	Stationary Sources	90	8.4.3.	Catalysts and Transfer Processes	104
7.5.3.	New Processes in Environmental Catalysis	90	9.	Catalyst Deactivation and Regeneration	104
7.6.	Energy Conversion	90	9.1.	Different Types of Deactivation	104
7.6.1.	Fuel Cells	90	9.2.	Catalyst Regeneration	105
7.6.2.	Catalytic Combustion	91	9.3.	Catalyst Reworking and Disposal	106
8.	Technology of Catalytic Processes	91	10.	References	106

1. Introduction

Catalysis is a phenomenon by which chemical reactions are accelerated by small quantities of foreign substances, called *catalysts*. A suitable *catalyst* can enhance the rate of a thermodynamically feasible reaction but cannot change the position of the thermodynamic equilibrium. Most catalysts are solids or liquids, but they may also be gases.

The catalytic reaction is a cyclic process. According to a simplified model, the reactant or reactants form a complex with the catalyst, thereby opening a pathway for their transformation into the product or products. Afterwards the catalyst is released and the next cycle can proceed.

However, catalysts do not have infinite life. Products of side reactions or changes in the catalyst structure lead to catalyst deactivation. In practice spent catalysts must be reactivated or replaced (see Chapter 9).

1.1. Types of Catalysis

If the catalyst and reactants or their solution form a common physical phase, then the reaction is called *homogeneously catalyzed*. Metal salts of organic acids, organometallic complexes, and carbonyls of Co, Fe, and Rh are typical *homogeneous catalysts*. Examples of *homogeneously*

catalyzed reactions are oxidation of toluene to benzoic acid in the presence of Co and Mn benzoates and hydroformylation of olefins to give the corresponding aldehydes. This reaction is catalyzed by carbonyls of Co or Rh.

Heterogeneous catalysis involves systems in the which catalyst and reactants form separate physical phases. Typical *heterogeneous catalysts* are inorganic solids such as metals, oxides, sulfides, and metal salts, but they may also be organic materials such as organic hydroperoxides, ion exchangers, and enzymes.

Examples of *heterogeneously catalyzed* reactions are ammonia synthesis from the elements over promoted iron catalysts in the gas phase and hydrogenation of edible oils on Ni–kieselguhr catalysts in the liquid phase, which are examples of *inorganic* and *organic catalysis*, respectively.

In *biocatalysis*, enzymes or microorganisms catalyze various biochemical reactions. The catalysts can be immobilized on various carriers such as porous glass, SiO₂, and organic polymers. Prominent examples of biochemical reactions are isomerization of glucose to fructose, important in the production of soft drinks, by using enzymes such as glucoamylase immobilized on SiO₂, and the conversion of acrylonitrile to acrylamide by cells of corynebacteria entrapped in a polyacrylamide gel.

The main aim of *environmental catalysis* is environmental protection. Examples are the re-

duction of NO_x in stack gases with NH_3 on $\text{V}_2\text{O}_5 - \text{TiO}_2$ catalysts and the removal of NO_x , CO, and hydrocarbons from automobile exhaust gases by using the so-called *three-way catalyst* consisting of Rh – Pt – $\text{CeO}_2 - \text{Al}_2\text{O}_3$ deposited on ceramic honeycombs.

The term *green catalytic processes* has been used frequently in recent years, implying that chemical processes may be made environmentally benign by taking advantage of the possible high yields and selectivities for the target products, with little or no unwanted side products and also often high energy efficiency.

The basic chemical principles of catalysis consist in the coordination of reactant molecules to central atoms, the ligands of which may be molecular species (homogeneous and biocatalysis) or neighboring atoms at the surface of the solid matrix (heterogeneous catalysis). Although there are differences in the details of various types of catalysis (e.g., solvation effects in the liquid phase, which do not occur in solid – gas reactions), a closer and undoubtedly fruitful collaboration between the separate communities representing homogeneous, heterogeneous, and biocatalysis should be strongly supported. A statement by David Parker (ICI) during the 21st Irvine Lectures on 24 April 1998 at the University of St. Andrews should be mentioned in this connection, namely, that, "... at the molecular level, there is little to distinguish between homogeneous and heterogeneous catalysis, but there are clear distinctions at the industrial level" [1].

1.2. Catalysis as a Scientific Discipline

Catalysis is a well-established scientific discipline, dealing not only with fundamental principles or mechanisms of catalytic reactions but also with preparation, properties, and applications of various catalysts. A number of academic and industrial institutes or laboratories focus on the study of catalysis and catalytic processes as well as on the improvement of existing and development of new catalysts.

International journals specializing in catalysis include *Journal of Catalysis*, *Journal of Molecular Catalysis* (Series A: Chemical; Series B: Enzymatic), *Applied Catalysis* (Series A: General; Series B: Environmental), *Reaction Ki-*

netics and Catalysis Letters, *Catalysis Today*, *Catalysis Letters*, *Topics in Catalysis*, *Advances in Organometallic Catalysis*, etc.

Publications related to catalysis can also be found in *Journal of Physical Chemistry*, *Langmuir*, and *Physical Chemistry Chemical Physics*.

Well-known serials devoted to catalysis are *Handbuch der Katalyse* [edited by G.-M. Schwab, Springer, Wien, Vol. 1 (1941) - Vol. 7.2 (1943)], *Catalysis* [edited by P.H. Emmett, Reinhold Publ. Co., Vol. 1 (1954) - Vol. 7 (1960)], *Catalysis – Science and Technology* [edited by J.R. Anderson and M. Boudart, Springer, Vol. 1 (1981) - Vol. 11 (1996)], *Catalysis Reviews* (edited by A.T. Bell and J.J. Carberry, Marcel Dekker), *Advances in Catalysis* (edited by B.C. Gates and H. Knözinger, Academic Press), *Catalysis* (edited by J.J. Spivey, The Royal Society of Chemistry), *Studies in Surface Science and Catalysis* (edited by B. Delmon and J.T. Yates), etc.

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- A comprehensive survey of the principles and applications: G. Ertl, H. Knözinger, J. Weitkamp (eds.), *Handbook of Heterogeneous Catalysis* with 5 Volumes and 2479 pages was published by VCH, Weinheim, 1997.
- The first *International Congress on Catalysis* (ICC) took place in 1956 in Philadelphia and has since been held every four years in Paris (1960), Amsterdam (1964), Moscow (1968), Palm Beach (1972), London (1976), Tokyo (1980), Berlin (1984), Calgary (1988), Budapest (1992), Baltimore (1996), Granada (2000). The 13th Congress will be held in Paris in 2004. Presented papers and posters have been published in the *Proceedings* of the corresponding congresses. The *International Congress on Catalysis Council* (ICC) was renamed at the Council meeting in Baltimore 1996. The international organization is now called *International Association of Catalysis Societies* (IACS).

In 1965 the *Catalysis Society of North America* was established and holds meetings in the USA every other year.

The *European Federation of Catalysis Societies* (EFCATS) was established in 1990. The *EUROPACAT* Conferences are organized under the auspices of EFCATS. The first conference took place in Montpellier (1993) followed by Maastricht (1995), Cracow (1997), Rimini (1999), and Limerick (2001).

Furthermore, every four years (in the even year between two International Congresses on Catalysis) an *International Symposium* focusing on *Scientific Basis for the Preparation of Heterogeneous Catalysts* held in Louvain-La Neuve (Belgium).

Other international symposia or congresses devoted to catalysis are: *International Zeolite Conferences*, *International Symposium of Catalyst Deactivation*, *Natural Gas Conversion Symposium*, *Gordon Conference on Catalysis*, *TOCAT (Tokyo Conference on Advanced Catalytic Science and Technology)*, *International Symposium of Acid-Base Catalysis*, the European conference series, namely the *Roermond*, *Sabatier* and *Schwab-conference*, and the *Taylor Conference*.

1.3. Industrial Importance of Catalysis

Because most industrial chemical processes are catalytic, the importance and economical significance of catalysis is enormous. More than 80 % of the present industrial processes established since 1980 in the chemical, petrochemical, and biochemical industries, as well as in the production of polymers and in environmental protection, use catalysts.

More than 15 international companies have specialized in the production of numerous catalysts applied in several industrial branches. In 1996 the turnover in the catalysts world market was estimated to be about $\$8 \times 10^9$ (see Chapter 4).

1.4. History of Catalysis

The phenomenon of catalysis was first recognized by BERZELIUS [2], [3] in 1835. However,

some catalytic reactions such as the production of alcoholic beverages by fermentation or the manufacture of vinegar by ethanol oxidation were practiced long before. Production of soap by fat hydrolysis and of diethyl ether by dehydration of ethanol belong to the catalytic reactions that were performed in the 16th and 17th centuries.

Besides BERZELIUS, MITSCHERLICH [3] was also involved at the same time in the study of catalytic reactions accelerated by solids. He introduced the term *contact catalysis*. This term for heterogeneous catalysis lasted for more than 100 years.

In 1895 OSTWALD [3], [4] defined catalysis as the acceleration of chemical reactions by the presence of foreign substances which are not consumed. His fundamental work was recognized with the Nobel prize for chemistry in 1909.

Between 1830 and 1900 several practical processes were discovered, such as flameless combustion of CO on a hot platinum wire, and the oxidation of SO₂ to SO₃ and of NH₃ to NO, both over Pt catalysts.

In 1912 SABATIER [3], [5] received the Nobel prize for his work devoted mainly to the hydrogenation of ethylene and CO over Ni and Co catalysts.

The first major breakthrough in industrial catalysis was the synthesis of ammonia from the elements, discovered by HABER [3], [6], [7] in 1908, using osmium as catalyst. Laboratory recycle reactors for the testing of various ammonia catalysts which could be operated at high pressure and temperature were designed by BOSCH [3]. The ammonia synthesis was commercialized at BASF (1913) as the *Haber-Bosch* [8] process. MITTASCH [9] at BASF developed and produced iron catalysts for ammonia production.

In 1938 BERGIUS [3], [10] converted coal to liquid fuel by high-pressure hydrogenation in the presence of an Fe catalyst.

Other highlights of industrial catalysis were the synthesis of methanol from CO and H₂ over ZnO-Cr₂O₃ and the cracking of heavier petroleum fractions to gasoline using acid-activated clays, as demonstrated by HOUDRY [3], [6] in 1928.

The addition of isobutane to C₃-C₄ olefins in the presence of AlCl₃, leading to branched C₇-C₈ hydrocarbons, components of high-quality aviation gasoline, was first reported by

IPATIEFF et al. [3], [7] in 1932. This invention led to a commercial process of UOP (USA).

Of eminent importance for Germany, which possesses no natural petroleum resources, was the discovery by FISCHER and TROPSCH [11] of the synthesis of hydrocarbons and oxygenated compounds from CO and H₂ over an alkalized iron catalyst. The first plants for the production of hydrocarbons suitable as motor fuel started up in Germany 1938. After World War II, Fischer-Tropsch synthesis saw its resurrection in South Africa. Since 1955 Sasol Co. has operated two plants with a capacity close to 3×10^6 t/a.

One of the highlights of German industrial catalysis before World War II was the synthesis of aliphatic aldehydes by ROELEN [12] by the addition of CO and H₂ to olefins in the presence of Co carbonyls. This homogeneously catalyzed reaction was commercialized in 1942 by Ruhr-Chemie and is known as Oxo Synthesis.

During and after World War II (till 1970) numerous catalytic reactions were realized on an industrial scale (see also Chapter 7). Some important processes are compiled in Table 1.

Table 2 summarizes examples of catalytic processes representing the current status of the chemical, petrochemical and biochemical industry as well as the environmental protection (see also Chapter 7).

2. Theoretical Aspects

The classical definition of a catalyst states that “a catalyst is a substance that changes the rate but not the thermodynamics of a chemical reaction” and was originally formulated by OSTWALD [4]. Hence, catalysis is a dynamic phenomenon.

As emphasized by BOUDART [16], the conditions under which catalytic processes occur on solid materials vary drastically. The reaction temperature can be as low as 78 K and as high as 1500 K, and pressures can vary between 10^{-9} and 100 MPa. The reactants can be in the gas phase or in polar or nonpolar solvents. The reactions can occur thermally or with the assistance of photons, radiation, or electron transfer at electrodes. Pure metals and multicomponent and multiphase inorganic compounds can act as catalysts. Site-time yields (number of product molecules formed per site and unit time) as low as 10^{-5} s^{-1} (corresponding to one turnover per

day) and as high as 10^9 s^{-1} (gas kinetic collision rate at 1 MPa) are observed.

It is plausible that it is extremely difficult, if not impossible, to describe the catalytic phenomenon by a general theory which covers the entire range of reaction conditions and observed site-time yields (reaction rates). However, there are several general *principles* which are considered to be laws or rules of thumb that are useful in many situations. According to BOUDART [16], the value of a principle is directly related to its generality. In contrast, *concepts* are more specialized and permit an interpretation of phenomena observed for special classes of catalysts or reactions under given reaction conditions.

In this chapter, important principles and concepts of heterogeneous catalysis are discussed, followed by a section on kinetics of heterogeneously catalyzed reactions. The chapter is concluded by a section on the determination of reaction mechanisms in heterogeneous catalysis.

2.1. Principles and Concepts

2.1.1. Sabatier's Principle

The Sabatier principle proposes the existence of an unstable intermediate compound formed between the catalyst surface and at least one of the reactants [5]. This intermediate must be stable enough to be formed in sufficient quantities and labile enough to decompose to yield the final product or products. The Sabatier principle is related to linear free energy relationships such as a Brønsted relation [16]. These relations deal with the heat of reaction q (thermodynamic quantity) and the activation barrier E (kinetic quantity) of an elementary step in the exothermic direction ($q > 0$). With an empirical parameter a ($0 < a < 1$) and neglecting entropy effects, a Brønsted relation can be written as

$$\Delta E = a \Delta q,$$

where ΔE is the decrease in activation energy corresponding to an increase Δq in the heat of reaction. Hence, an elementary step will have a high rate constant in the exothermic direction when its heat of reaction q increases. Since the activation barrier in the endothermic direction is equal to the sum of the activation energy E

Table 1. Important catalytic processes commercialized during and after World War II (until 1970) [3], [6]

Year of commercialization	Process	Catalyst	Products
1939 – 1945	dehydrogenation	Pt – Al ₂ O ₃	toluene from methylcyclohexane
	dehydrogenation	Cr ₂ O ₃ – Al ₂ O ₃	butadiene from <i>n</i> -butane
	alkane isomerization	AlCl ₃	<i>i</i> -C ₇ – C ₈ from <i>n</i> -alkanes
1946 – 1960	oxidation of aromatics	V ₂ O ₅	phthalic anhydride from naphthalene and <i>o</i> -xylene
	hydrocracking	Ni – aluminosilicate	fuels from high-boiling petroleum fractions
1961 – 1970	polymerization (Ziegler – Natta)	TiCl ₄ – Al(C ₂ H ₅) ₃	polyethylene from ethylene
	dehydrogenation	Fe ₂ O ₃ – Cr ₂ O ₃ – KOH	styrene from ethylbenzene
	oxidation (Wacker process)	PdCl ₂ – CuCl ₂	acetaldehyde from ethylene
	steam reforming	Ni – α -Al ₂ O ₃	Co, (CO ₂), and H ₂ from methane
	ammonoxidation	Bi phosphomolybdate	acrylonitrile from propene
	fluid catalytic cracking	H zeolites + aluminosilicates	fuels from high boiling fractions
	reforming	bimetallic catalysts (Pt, Sn, Re, Ir)	gasoline
	low-pressure methanol synthesis	Cu – ZnO – Al ₂ O ₃	methanol from CO, H ₂ , CO ₂
	isomerization	enzymes immobilized on SiO ₂	fructose from glucose (production of soft drinks)
	distillate dewaxing	ZSM-5, mordenites	removal of <i>n</i> -alkanes from gasoline
	hydrorefining	Ni –, CO – MoS _x	hydrodesulfurization, hydrodenitrification

Table 2. Important catalytic processes commercialized after 1970 [6], [7], [13–15]

Year of commercialization	Process	Catalyst	Product
1971 – 1980	automobile emission control	Pt – Rh – CeO ₂ – Al ₂ O ₃ (three-way catalyst)	removal of NO _x , CO, CH _x
	carbonylation (Monsanto process)	organic Rh complex	acetic acid from methanol
1981 – 1985	MTG (Mobil process)	zeolite (ZSM-5)	gasoline from methanol
	alkylation (Mobil – Badger)	modified zeolite (ZSM-5)	ethylbenzene from ethylene
	selective catalytic reduction (SCR; stationary sources)	V Ti (Mo, W)oxides (monoliths)	reduction of NO _x with NH ₃ to N ₂
	esterification (MTBE synthesis)	ion-exchange resin	methyl- <i>tert</i> -butyl ether from isobutene + methanol
	oxidation (Sumitomo Chem., 2-step process)	1. Mo, Bi oxides	acrylic acid from propene
	oxidation (Monsanto)	2. Mo, V, PO (heteropolyacids)	maleic anhydride from <i>n</i> -butane
	fluid-bed polymerization (Unipol)	vanadylphosphate	polyethylene and polypropylene
	hydrocarbon synthesis (Shell)	Ziegler – Natta type	
		1. Co – (Zr,Ti) – SiO ₂	middle distillate from CO + H ₂
		2. Pt – SiO ₂	deodorization
1986 –	environmental control (combustion process)	Pt – Al ₂ O ₃ (monoliths)	
	oxidation with H ₂ O ₂ (Enichem)	Ti silicalite	hydroquinone and catechol from phenol
	hydration	enzymes	acrylamide from acrylonitrile
	ammonoxidation (Montedipe)	Ti silicalite	cyclohexanone oxime from cyclohexanone, NH ₃ , and H ₂ O ₂
	dehydrogenation of C ₃ , C ₄ alkanes (Star and Oleflex processes)	Pt(Sn) – zinc aluminate, Pt – Al ₂ O ₃	C ₃ , C ₄ olefins

and the heat of reaction, the rate constant will decrease with increasing q .

The Brønsted relationship represents a bridge between thermodynamics and kinetics and, together with the Sabatier principle, permits an interpretation of the so-called *volcano plots* first reported by BALANDIN [17]. These volcano curves result when a quantity correlated with the

rate of reaction under consideration is plotted against a measure of the stability of the intermediate compound. The latter quantity can be the heat of adsorption of one of the reactants or the heat of formation of a bulk compound relative to the surface compound, or even the heat of formation of any bulk compound that can be correlated with the heat of adsorption, or sim-

ply the position of the catalytic material (metal) along a horizontal series in the Periodic Table [16].

As an example, Figure 1 shows the volcano plot for the decomposition of formic acid on transition metals [18]. The intermediate in this reaction was shown to be a surface formate. Therefore, the heats of formation ΔH_f of the bulk metal formates were chosen as the measure of the stability of the intermediate. At low values of ΔH_f , the reaction rate is low and corresponds to the rate of adsorption, which increases with increasing heat of formation of the bulk formates (representing the stability of the surface compound). At high values of ΔH_f the reaction rate is also low and corresponds to the desorption rate, which increases with decreasing ΔH_f . As a consequence, a maximum in the rate of reaction (decomposition of formic acid) is observed at intermediate ΔH_f values which is neither a pure rate of adsorption nor a pure rate of desorption but which depends on both.

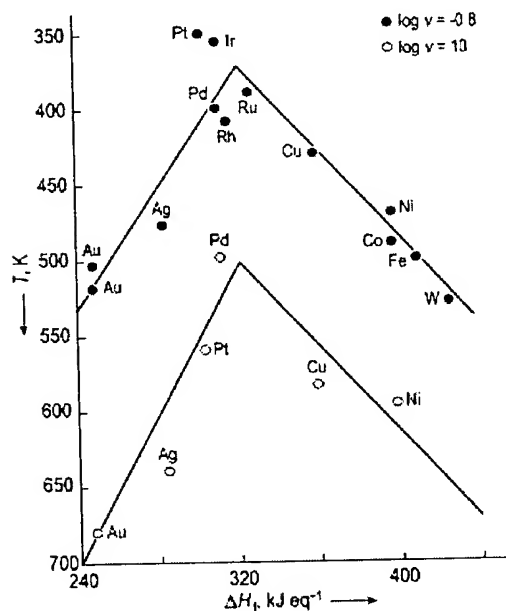


Figure 1. Volcano plot for the decomposition of formic acid. The temperature T at which the rate of decomposition v has a fixed value is plotted against the heat of formation ΔH_f of the metal formate (adopted from [28]).

2.1.2. The Principle of Active Sites

The Sabatier principle of an unstable surface intermediate requires chemical bonding of reactants to the catalyst surface, most likely between atoms or functional groups of reactant and surface atoms. This leads to the *principle of active sites*. When LANGMUIR formulated his model of chemisorption on metal surfaces [19], he assumed an array of sites which were energetically identical and noninteracting, and which would adsorb just one molecule from the gas phase in a localized mode. The Langmuir adsorption isotherm results from this model. The sites involved can be considered to be active sites.

LANGMUIR was already aware that the assumption of identical and noninteracting sites was an approximation which would not hold for real surfaces, when he wrote [20]: "Most finely divided catalysts must have structures of great complexity. In order to simplify our theoretical consideration of reactions at surfaces, let us confine our attention to reactions on plane surfaces. If the principles in this case are well understood, it should then be possible to extend the theory to the case of porous bodies. In general, we should look upon the surface as consisting of a checker-board." LANGMUIR thus formulated the surface science approach to heterogeneous catalysis for the first time.

The heterogeneity of active sites on solid catalyst surfaces and its consequences were emphasized by TAYLOR [21], who recognized that "There will be all extremes between the case in which all atoms in the surface are active and that in which relatively few are so active." In other words, exposed faces of a solid catalyst will contain terraces, ledges, kinks, and vacancies with sites having different coordination numbers. Nanoscopic particles have edges and corners which expose atoms with different coordination numbers [22]. The variation of coordination numbers of surface atoms will lead to different reactivities and activities of the corresponding sites. In this context, Schwab's adlineation theory may be mentioned [23], which speculated that one-dimensional defects consisting of atomic steps are of essential importance. This view was later confirmed by surface science studies on stepped single-crystal metal surfaces [24].

In addition to variable coordination numbers of surface atoms in one-component solids, the surface composition may be different from that of the bulk and different for each crystallographic plane in multicomponent materials (*surface segregation* [25]). This would lead to a heterogeneity of the local environment of a surface atom and thus create nonequivalent sites.

Based on accurate kinetic measurements and on the Taylor principle of the existence of inequivalent active sites, BOUDART et al. [26] coined the terms *structure-sensitive* and *structure-insensitive reactions*. A truly structure-insensitive reaction is one in which all sites seem to exhibit equal activity on several planes of a single crystal. Surprisingly, many heterogeneously catalyzed reactions turned out to be structure-insensitive. Long before experimental evidence for this phenomenon was available and before a reliable interpretation was known, TAYLOR predicted it by writing [21]: "The amount of surface which is catalytically active is determined by the reaction catalyzed." In other words, the surface of a catalyst adapts itself to the reaction conditions for a particular reaction. The driving force for this reorganization of a catalyst surface is the minimization of the surface free energy, which may be achieved by *surface-reconstruction* [27], [28]. As a consequence, a meaningful characterization of active sites requires experiments under working (in situ) conditions of the catalytic system.

The principle of active sites is not limited to metals. Active sites include metal cations, anions, Lewis and Brønsted acids, acid–base pairs (acid and base acting simultaneously in chemisorption), organometallic compounds, and immobilized enzymes. Active sites may include more than one species (or atom) to form multiplets [17] or ensembles [29]. A mandatory requirement for these sites to be active is that they are accessible for chemisorption from the fluid phase. Hence, they must provide free coordination sites. Therefore, BURWELL et al. [30], [31] coined the term *coordinatively unsaturated sites* in analogy with homogeneous organometallic catalysts. Thus, active sites are to be considered as atoms or groups of atoms which are embedded in the surface of a matrix in which the neighboring atoms (or groups) act as ligands. *Ensemble and ligand effects* are discussed in detail by SACHTLER [32] and quantum chem-

ical treatments of geometric ensemble and electronic ligand effects on metal alloy surfaces are discussed by HAMMER and NØRSKOV [33].

2.1.3. Surface Coordination Chemistry

The surface complexes formed by atoms or molecules are now known to usually resemble a local structure similar to molecular coordination complexes. The bonding in these surface complexes can well be described in a localized picture [34], [35]. Thus, important phenomena occurring at the surface of solid catalysts may be described in the framework of *surface coordination chemistry* or *surface organometallic chemistry* [36], [37].

This is at variance with the so-called *band theory* of catalysis, which attempted to correlate catalytic performance with bulk electronic properties [38–40]. The shortcomings of this theory in oxide catalysis are discussed by STONE [41].

2.1.4. Modifiers and Promoters

The performance of real industrial catalysts is often adjusted by *modifiers* (additives) [42], [43]. A modifier is called a *promoter* when it increases the catalyst activity in terms of reaction rate per site. Modifiers may also affect a catalyst's performance in an undesired manner. In this case the modifier acts as a catalyst *poison*. However, this simple distinction between promoters and poisons is less straightforward for reactions yielding more than one product in parallel or consecutive steps, of which only one is the desired product. In this case not only high activity but high selectivity is desired. The selectivity can be improved by adding substances that poison undesirable reactions. In exothermic reactions excessively high reaction rates may lead to a significant temperature increase (sometimes only locally: hot spots) which can yield undesirable products (e.g., CO and CO₂ in selective catalytic oxidation). A deterioration of the catalyst due to limited catalyst stability may also occur. Consequently, a modifier is required which decreases the reaction rate so that a steady-state temperature and reaction rate can be maintained. Although the modifier acts as a poison in these cases, it is in fact a promoter as far as selectivity and catalyst stability are concerned.